

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
3 May 2001 (03.05.2001)

PCT

(10) International Publication Number  
**WO 01/30953 A1**

(51) International Patent Classification<sup>7</sup>: C11D 3/00, 17/00, 11/00

(74) Agents: REED, T., David et al.: The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).

(21) International Application Number: PCT/US00/29294

(22) International Filing Date: 23 October 2000 (23.10.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
9925481.5 28 October 1999 (28.10.1999) GB

(71) Applicant (for all designated States except US): **THE PROCTER & GAMBLE COMPANY** [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **RIDYARD, Mark, William** [GB/GB]; 20 Armstrong Avenue, Heaton, Newcastle upon Tyne NE6 5RD (GB). **KATSUDA, Rinko** [JP/JP]; Kobe Park City C507, 6-2-1, Minatojima naka machi, Chuo-ku, Kobe, Hyogo 650-0046 (JP). **HILDAGO, Noe, Ongcoy** [PH/JP]; 1-1-141-1016 Koyo-cho Naka, Higashinada-ku, Kobe 658-0032 (JP).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, EE, ES, FI, FR, GB, GR, GU, HK, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MY, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW). Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM). European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DETERGENT COMPOSITIONS

(57) Abstract: A detergent composition comprises an effervescence particle which releases gas on contact with water either due to a reaction which takes place with water or due to release of a gas on contact with water. The composition may contain a detergent matrix having eRH below 30 %. The detergent matrix comprises a detergent matrix component which is preferably a spray dried particle, and optional additional detergent ingredients.

WO 01/30953 A1

## Detergent Compositions

### 5 Field of the Invention

This invention relates to compositions which need to dissolve readily and rapidly in an aqueous medium. The technology may find application in various fields such as cleaning compositions, in particular laundry and dishwashing detergent compositions which may be in a granular form or which may have undergone additional processing steps to be in a tablet form. The invention relates particularly to laundry detergent applications.

### Background of the Invention

Poor dissolution and dispensing problems are well-known in the detergent field. This problem has been exacerbated by recent tendencies to produce higher bulk density detergents, such as above 600g/l, to meet the consumer need for lower product and packaging volumes and less wastage i.e. higher active cleaning compositions. The problem is compounded by the use of detergent formulations which are based not on readily soluble phosphate builders, but instead on less soluble alternatives which overcome any environmental problems associated with phosphate builders. In addition, there is an increased need to promote rapid release of detergents into the wash water to provide greatest cleaning performance in short, energy-efficient wash cycles where the time of contact of the detergent solution with the items to be washed may be reduced to a minimum. Many solutions have been proposed to try to avoid the problems of poor dissolution and dispensing.

25 One such solution has been the use of effervescent systems in detergents. For example, detergent compositions comprising effervescing ingredients are described in WO98/04687. In WO98/04671, effervescence systems for use in detergents are disclosed in which in an effort to improve dissolution, acid and alkaline effervescing reactants which react on contact with water to produce a gas, are mixed with a stabilising agent to produce a substantially anhydrous effervescence particle which has maximum efficacy on use in a washing step. Similarly, WO98/35011 also discloses particles comprising sodium bicarbonate and organic acid reactants which react together and

which are formed into a particle with a binder. EP-A-918 087 describes co-builder particles for adding to detergent compositions, comprising bicarbonate and polycarboxylic acid which are formed by roller-compaction and which contain no free moisture. However, the requirements of providing good storage stability and good end  
5 use effervescence on contact with the wash liquor are conflicting requirements; the use of stabilising agents can prevent or reduce efficacy in the wash conditions as the water contact with the effervescing reactants and the resulting reaction rate slows down, so that the effervescing and therefore, dissolution aid effect is undesirably reduced.

#### Summary of the Invention

10 The present inventors have found that these problems can be overcome so that a readily dissolving detergent composition which has good dissolution properties on contact with the wash water can be provided by a detergent composition consisting essentially of an effervescence particle and a detergent matrix, characterised in that the detergent matrix has an eRH of no greater than 30 %.

15 In a preferred aspect of the invention, the effervescence particle has a moisture pick up of no greater than 3% as measured at 60% RH and at 25°C to moisture equilibrium.

The present invention also encompasses a process of manufacturing a detergent composition comprising a detergent matrix and an effervescence particle, the detergent  
20 matrix comprising a detergent matrix component and optional additional detergent ingredients, the process comprising forming a detergent matrix component comprising surfactant and solid component by agglomeration and/or spray drying and submitting the detergent matrix component to a drying step, combining the detergent matrix component and other optional additional detergent ingredients with the effervescence particle,  
25 wherein the eRH of the detergent matrix is below 30%.

The present invention also encompasses a process of manufacturing such detergent compositions comprising forming a detergent matrix component comprising surfactant and solid component by agglomeration and/or spray drying and submitting the detergent matrix component to a drying step in which the free moisture of the detergent  
30 matrix component is reduced to below 3 wt% and then mixing the detergent matrix component and other optional additional detergent ingredients with an effervescence

particle. Preferably, the free moisture in any optional additional detergent ingredients is also below 3 wt%.

In accordance with a further aspect of the invention there is provided a detergent composition comprising an effervescence particle and a low density detergent matrix component having a bulk density below 400 g/l. Preferably, in addition, the median particle size of the low density detergent matrix component is from 50 to 500 $\mu$ m.

In accordance with a further aspect of the invention, a different composition is provided which comprises an effervescence particle and detergent matrix component having a bulk density from 400 to 800 g/l (small particle size), the median particle size of the small particle size detergent matrix component being from 50 to 300  $\mu$ m.

In accordance with the present invention there is also provided use of a detergent composition in a washing process in which the detergent composition is contacted with water for laundering household items, preferably laundry.

#### Detailed Description of the Invention

##### 15 Effervescence Particle

The effervescence particle comprises one or more effervescence components such that on contact of the effervescence particle with water, effervescence is produced. This effervescence may be as a result of gas trapped in the matrix of the particle being released when the particle contacts water, or more usually, is the result of a reaction which takes place between two or more reactants present in the effervescence particle which, on contact with water react with one another to produce a gas.

Where the effervescence is produced by reaction of two or more reactants, preferably, the reactants are provided by an acid-source and an alkali-source. Suitable acid sources include solid organic, mineral or inorganic acids, salts or derivatives thereof or mixtures thereof. It may be preferred that the acids are mono-, bi- or tri-protonic acids. Such acids include mono- or polycarboxylic acids preferably citric acid, adipic acid, glutaric acid, 3-chetoglutaric acid, citramalic acid, tartaric acid, maleic acid, fumaric acid, malic acid, succinic acid, malonic acid. Such acids are preferably used in their acidic form. Derivatives also include esters of the acids. Preferred acids include citric acid and malic acid. Citric acid is particularly preferred.

The acid-source is preferably present in the effervescence particles at a level of from 0.1% to 99% by weight of the total particle, preferably from 3% to 80%, more

preferably from 10% to 75% and most preferably from 15% to 70%. It may be preferred for at least 80 wt% of the acid-source to have a particle size of from about 150  $\mu\text{m}$  to about 1200 $\mu\text{m}$ , or up to 1000 $\mu\text{m}$  or 710 $\mu\text{m}$ . However, generally it is preferred for at least 80 wt% of the acid source to have a particle size greater than 100 $\mu\text{m}$ , preferably  
5 greater than 200 $\mu\text{m}$ .

Any alkali-source may be used in the effervescence particle. Carbonate alkali-sources are particularly preferred, for example including carbonate, bicarbonate, sesquicarbonate and percarbonate salts, in particular bicarbonate and/or carbonate. Preferred carbonates to be used herein include carbonate and hydrogen carbonates which  
10 should be present in the effervescence particle in a from which can react with the acid-source. Generally, therefore, the alkali-source should be water soluble, or of very fine particle size such that a reaction with the acid-source takes place readily on contact of the effervescence particle with water. Salts of alkali metals or alkaline earth metals are suitable. Water-soluble salts such as salts of potassium, lithium, sodium, and the like are  
15 preferred amongst which sodium and potassium carbonate are particularly preferred. Suitable bicarbonates to be used herein include any alkali metal salt of bicarbonate like lithium, sodium, potassium and the like, amongst which sodium and potassium bicarbonate are preferred. Bicarbonate may be preferred to carbonate, because it is more-weight effective, i.e., at parity weight bicarbonate is a larger  $\text{CO}_2$  "reservoir" than  
20 carbonate. However, overall detergent formulation requirements may result in the more alkaline pH, produced by carbonates, providing a more useful overall detergent formulation, thus the choice of carbonate or bicarbonate or mixtures thereof in the effervescence granules may depend on the pH desired in the aqueous medium wherein the detergent composition comprising the effervescence particles is dissolved. For  
25 example where a relatively high pH is desired in the aqueous medium (e.g., above pH 9.5) it may be preferred to use carbonate alone or to use a combination of carbonate and bicarbonate wherein the level of carbonate is higher than the level of bicarbonate, typically in a weight ratio of carbonate to bicarbonate from 0.1 to 10, more preferably from 1 to 5 and most preferably from 1 to 2. In one aspect of the invention, where the  
30 detergent composition comprises bicarbonate alone as the alkali-source, preferably the effervescence particle additionally comprises greater than 6 wt% citric acid optionally in mixtures with other acid-source components.

The carbonate source is preferably present in the effervescence particles at a level of from 0.1% to 99% by weight of the total, preferably from 20% to 95%, more preferably from 30% to 85% and most preferably from 35% to 75% by weight of the effervescence particle. Preferably, at least 80 wt% or more of the carbonate source has a particle size in the range of from about 2  $\mu\text{m}$  to about 1200 $\mu\text{m}$  or even from 2  $\mu\text{m}$  to 1000  $\mu\text{m}$ . It may be preferred for the alkali-source to have a particle size such that 80 wt% of the alkali source has a particle size below 50 microns. For optimum effervescence in aqueous medium the molar ratio of reactive groups of the acid-source to alkali-source, the alkali-source preferably comprising carbonate and/or bicarbonate, is preferably substantially stoichiometric, for example from 5:1 to 1:5, more preferably from 3:1 to 1:3, and most preferably from 3:2 to 2:3.

Preferably the effervescence particle is substantially anhydrous such that the overall moisture content (including both bound i.e. water of crystallisation, and unbound i.e. free moisture) is less than 0.5 wt% of the effervescence particle. More particularly, where the effervescence component comprises both acid-source and alkali-source, preferably at least the acid-source used for forming the effervescence particle has an overall moisture content less than 0.1 wt%, more preferably less than 0.05 wt% and most preferably less than 0.01 wt%. More preferably, the alkali-source also has an overall moisture content less than 0.5 or less than 0.1wt%, more preferably less than 0.05 wt% and most preferably less than 0.01 wt%.

Preferably, the effervescence particles have a particle size such that the median particle size is from 0.001 mm to 7 mm, preferably less than 2 mm. Preferably the span is less than 2, more preferably less than 1.5.

As used herein, the phrase "median particle size" means the geometric mass median diameter of a set of discrete particles as measured by any standard mass-based particle size measurement technique, preferably by dry sieving. As used herein, the phrase "geometric standard deviation" or "span" of a particle size distribution means the geometric breadth of the best-fitted log-normal function to the above-mentioned particle size data which can be accomplished by the ratio of the diameter of the 84.13 percentile divided by the diameter of the 50<sup>th</sup> percentile of the cumulative distribution ( $D_{84.13}/D_{50}$ ); See Gotoh et al, *Powder Technology Handbook*, pp. 6-11, Marcel Dekker 1997.

The bulk density of the effervescence particles is preferably from 500 g/l to 1200 g/l, more preferably from 700 g/l to 1100 g/l.

The effervescence particles may optionally comprise additional ingredients. Generally, the effervescence particles comprise no more than 50 wt% of the particle of additional ingredient(s), preferably no more than 35 wt% and more preferably no more than 20% or 10%. It may be particularly preferred to have a highly active particle comprising no more than 5 wt% or even no more than 2 wt% of additional ingredients besides the components which contribute to the gas production/release. Suitable additional ingredients may comprise any detergent ingredients which are described below. Particularly suitable are surfactants or organic or inorganic builder components, preferably those which are water soluble such as those described below.

Although not preferred for the reasons given above, optional binders or coating agents may be incorporated into the effervescence particles. Suitable materials are selected from one or mixtures of more than one of the binders and coating materials known to those skilled in the art. In particular suitable binders include anionic surfactants like C6-C20 alkyl or alkylaryl sulphonates or sulphates, preferably C8-C20 alkylbenzene sulphonates, cellulose derivatives such as carboxymethylcellulose and homo- or copolymeric polycarboxylic acid or their salts, nonionic surfactants, preferably C10-C20 alcohol ethoxylates containing from 5-100 moles of ethylene oxide per mole of alcohol and more preferably the C15-C20 primary alcohol ethoxylates containing from 20-100 moles of ethylene oxide per mole of alcohol. Of these tallow alcohol ethoxylated with 25 moles of ethylene oxide per mole of alcohol (TAE25) or 50 moles of ethylene oxide per mole of alcohol (TAE50) are preferred. Other preferred binders include the polymeric materials like polyvinylpyrrolidones with an average molecular weight of from 12 000 to 700 000 and polyethylene glycols with an average weight of from 600 to 10 000. Copolymers of maleic anhydride with ethylene, methylvinyl ether, methacrylic acid or acrylic acid are other examples of polymeric binders. Other binders further include C10-C20 mono and diglycerol ethers as well as C10-C20 fatty acids. In the embodiment of the present invention where a binder is desired C8-C20 alkylbenzene sulphonates are particularly preferred.

The effervescence particles used in the present invention are preferably prepared by mixing the effervescence component(s) which contribute to gas production/release,

with any additional ingredients to produce an intimate mixture and then submitting the mixture to a granulation step to form particles. Any granulation process may be used, however, in order to maintain high active levels in the finished effervescence particles, the granulation should preferably take place substantially without addition of any free  
5 moisture to the mixture. A preferred agglomeration step comprises a pressure agglomeration step to form an agglomerate mixture, followed if necessary by a granulation step in which the agglomerate is formed into the effervescence particles for use in the detergent compositions of the invention.

In the preferred pressure agglomeration process, the substantially dry mixture  
10 comprising the effervescence components and any optional additional ingredients is exposed to high external forces that bring the particles closely together thereby densifying the bulk mass of said particles and creating binding mechanisms between the components in the mixture. Indeed, pressure agglomeration results in an aggregation mechanism which is characterised by the presence of inter-particle bonds between  
15 primary solid effervescent particles and a structure in which these effervescence particles are still identifiable and retain many of their characteristics, e.g. the ability to react together in presence of water to deliver carbon dioxide.

The increase of density associated with the preferred processes for making the effervescence particles for use in the present invention, is closely linked to the pressure  
20 applied. Typically, the bulk density will increase up to 200g/l, preferably from 10 g/l to 150 g/l, starting from the density of the mixture comprising the effervescent raw materials, i.e., acid and the carbonate source, and optionally the binder, before having undergone a pressure agglomeration.

Pressure agglomeration may be carried out using different processes which can be  
25 classified by the level of forces applied. A preferred process to be used herein is roller compaction. In this process the effervescence components, preferably the acid-source and the alkali-source and any optional additional ingredients after having been mixed together are forced between two compaction rolls that applies a pressure to said mixture so that the rotation of the rolls transforms the mixture into a compacted sheet/flake. This  
30 compacted sheet/flake is then broken up to form effervescence particles.

Typical roller compactors for use herein are for example Pharmapaktor L200/50P  
® commercially available from Hosokawa Bepex GmbH. The process variables during



the pressure agglomeration step via roller compaction are the distance between the rolls, the feed rate, the compaction pressure and the roll speed. A typical feeding device is a feed screw. The distance between the rolls is typically from 0.5 cm to 10 cm, preferably from 3 to 7 cm, more preferably from 4 to 6 cm. The pressing force is typically between  
5 20 kN and 120 kN, preferably from 30 kN to 100kN, more preferably from 50 kN to 100 kN. Typically, the roll speed is between 1 rpm and 180 rpm, preferably from 2 rpm to 50 rpm and more preferably from 2 rpm to 35 rpm. Typically, the feed rate is between 1 rpm and 100 rpm, preferably from 5 rpm to 70 rpm, more preferably from 8 rpm to 50 rpm. Temperature at which compaction is carried out is not critical, typically it varies from 0°  
10 C to 40 °C.

The sheet/flake produced by the pressure agglomeration process is broken up into effervescence particles by any suitable method for reducing the size of the sheet/flake to form particles, for example, by cutting, chopping or breaking the sheet/flake to produce the required length, and if necessary, by a process to make the particles rounded i.e. to  
15 obtain round or spherical granules according to the diameter size as defined herein before. In the preferred embodiment one way to break up the sheet/flake after the roller compaction step is to mill the compacted flake/sheet. Milling may typically be carried out with a Flake Crusher FC 200® commercially available from Hosokawa Bepex GmbH.

Depending on the particle size required for the effervescence particles, the milled  
20 material may be sieved further. Such a sieving of the dry effervescent granules can be carried out, for example with a commercially available Alpine Airjet Screen ®.

#### Detergent Matrix

The present inventors have found that for stability and maximum efficacy of effervescence in water in the wash conditions, it is not simply the properties of the  
25 effervescence particle which are critical. Thus, by careful selection and processing of the detergent matrix itself, improved properties can be achieved. This enables binders, which may adversely affect dissolution rates of the effervescence particle, to be used in reduced amounts or preferably omitted altogether.

Thus, in accordance with the present invention, the detergent matrix which  
30 comprises a pre-formed detergent matrix component comprising surfactant, and optional additional detergent ingredients, has an eRH no greater than 30%. Preferably the eRH is no greater than 25%, more preferably no greater than 20% or even no greater than 15% or

12% or even 10%. The eRH is measured using a Rotronic™ Hygroskop DT calibrated according to the manufacturers instructions as set out in the Rotronic Hygroskop application leaflet 2/E Spi/S dated 3.1.83, using defined saturated salt solutions which cover the humidity range to be tested. All measurements are taken at 25°C.

5           The low eRH of the detergent matrix has a surprising effect on the stability of the effervescence particles. Whilst not wishing to be bound by theory, it is believed that this is because the detergent matrix not only does not contribute moisture to the effervescence particle leading to release of effervescence on storage, but in addition acts as a moisture sink so that moisture from the atmosphere contacting the detergent on storage, has a  
10   diminished adverse effect on the stability of the effervescence particle.

          Although there is not necessarily a direct correlation between free moisture content and eRH, preferably the detergent matrix has a free moisture content of no greater than 2wt%, preferably no greater than 1 wt%, and even more preferably no greater than 0.5 or 0.1 or 0.05 wt%. This low free moisture content may be achieved by drying one or  
15   more than one, or all of the components in the detergent matrix. Thus the detergent matrix component and one or more optional additional ingredients may be pre-mixed before drying or may be dried after mixing. Additional detergent matrix component and/or optional additional ingredients may then be combined with these pre-dried components without an additional drying step. However, the overall eRH of the  
20   detergent matrix (all those ingredients in the detergent composition with the exception of the effervescence particle) should be below 30%. Preferably in addition, the free moisture content of the detergent matrix should be below 2wt% or even 1wt% or 0.5 or 0.01 wt%.

          In a preferred aspect of the invention, at least one of the components in the  
25   detergent matrix is over-dried i.e. has been dried to a level such that water which is bound to one or more of the detergent ingredients either in the detergent matrix component or optional additional detergent ingredients, is removed.

          In accordance with a further aspect of the invention, there is provided a detergent composition comprising an effervescence particle and a low density detergent matrix  
30   component having a bulk density below 400g/l.

#### Detergent Matrix Component

The detergent matrix comprises a detergent matrix component. Such component comprises a pre-formed particulate which may be in the form of a powder, particle, flake or other solid form, comprising surfactant and optional additional detergent ingredients.

The surfactant may be anionic, nonionic, cationic, amphoteric, zwitterionic or mixtures thereof. Preferred detergent matrix components comprise anionic, nonionic and/or cationic surfactants. In particular matrix components which comprise anionic surfactant may be particularly useful. Suitable surfactants are described in more detail below. The surfactant content of a pre-formed matrix component is preferably from 5 to 80 % by weight of the matrix component. Amounts of surfactants above 10% by wt or even above 20 wt% or above 30 wt%, based on the total weight of the detergent matrix component, may be preferred. Amounts of surfactant below 70% or even below 50% may be preferred.

The detergent matrix component generally also comprises a solid material which may be filler such as sulphates, in particular sodium sulphate, but more preferably the detergent matrix component comprises at least one detergent ingredient, in particular, builder or alkalinity components, or mixtures of such components. Suitable examples include phosphate, aluminosilicate, crystalline layered silicates, sodium carbonate or amorphous silicates. These materials are described below in more detail. For example, each of these components individually, or in mixtures may be present in amounts above 5%, preferably above 10% or even above 20% by weight of the content of the pre-formed matrix component. Particularly preferred builder components are sodium carbonate and/or zeolite. Zeolite A and zeolite MAP are both suitable.

A pre-formed matrix component preferably also comprises an organic builder such as a poly carboxylic acid and/or salt such as citric acid, tartaric acid, malic acid, succinic acid and their salts or a polymeric polycarboxylate such as polymers based on acrylic acids or maleic acids or co-polymers thereof. Such components are generally present in the matrix component at levels below 15 wt %, preferably below 10 wt % of the matrix component.

Other preferred ingredients in the pre-formed matrix component are optical brighteners or chelants such as phosphonate chelants NTA, DTPA and succinic acid derivative chelants, as described below. These components are preferably present in a

pre-formed particulate component in amounts below 5 wt % or even below 2 wt % of the matrix component.

The detergent matrix may comprise one or more pre-formed detergent matrix components. Suitable pre-formed components may have been formed by spray-drying, agglomeration, marumerisation, extrusion or compaction, all of which methods for combining detergent ingredients are well-known in the art. Particularly preferred pre-formed matrix components are powders obtained from spray-drying processes, agglomerates and extrudates. Spray-dried powders are particularly useful. Detergent matrix components made according to at least one low shear mixing step, for example in a fluidised bed, for example by fluid bed agglomeration are also preferred.

Suitable spray-drying processes for forming such pre-formed detergent matrix components are described for example in EP-A-763594 or EP-A-437888. Suitable processes for forming detergent matrix components which are agglomerates are described for example in WO93/25378, EP-A-367339, EP-A-420317 or EP-A-506184. Suitable moderate to low shear mixers may be for example a Lodige KM (trademark) (Ploughshare) moderate speed mixer, or mixer made by Fukae, Draes, Schugi or similar brand mixers which mix with only moderate to low shear. The Lodige KM (ploughshare) moderate speed mixer which is a preferred mixer for use in the present invention comprises a horizontal hollow static cylinder having a centrally mounted rotating shaft around which several plough-shaped blades are attached. Preferably, the shaft rotates at a speed of from about 15 rpm to about 140 rpm, more preferably from about 80 rpm to about 120 rpm. The grinding or pulverizing is accomplished by cutters, generally smaller in size than the rotating shaft, which preferably operate at about 3600 rpm. Other mixers similar in nature which are suitable for use in the process include the Lodige Ploughshare™ mixer and the Drais® K-T 160 mixer. Generally, in the processes of the present invention, the shear will be no greater than the shear produced by a Lodige KM mixer with the tip speed of the ploughs below 10 m/s, or even below 8m/s or even lower.

Preferably, the mean residence time of the various starting detergent ingredients in the low or moderate speed mixer is preferably in range from about 0.1 minutes to about 15 minutes, most preferably the residence time is about 0.5 to about 5 minutes. In this way, the density of the resulting detergent agglomerates is at the desired level.

Other suitable mixers for use in the present invention are low or very low shear mixers such as rotating bowl agglomerators, drum agglomerators, pan agglomerators and fluid bed agglomerators.

Fluid bed agglomerators are particularly preferred. Typical fluidised bed  
5 agglomerators are operated at a superficial air velocity of from 0.4 to 4 m/s, either under positive or negative pressure. Inlet air temperatures generally range from -10 or 5°C up to 250°C. However inlet air temperatures are generally below 200°C, or even below 150°C. Suitable processes using a fluid bed agglomerator are described for example in WO98/58046 or WO99/03964. Suitable processes for forming detergent matrix  
10 components by extrusion are described for example in WO91/02047.

The detergent matrix may comprise only one pre-formed component as described or it may comprise a mixture of components, for example mixtures of different spray dried powders or of different agglomerates etc or mixtures of combinations of agglomerates, spray dried powders and/or extrudates etc. as described above. In order to  
15 obtain a detergent matrix having the desired low eRH, the detergent matrix component or mixture thereof, will have undergone drying to provide the required low moisture content. Such drying may be provided in any conventional drying step, or may be the result of more thorough drying than is conventional using the usual processing route. For example, in the spray drying process the spray drying tower may be operated at higher air  
20 inlet temperatures for example from 300°C to 350°C or even 400°C. Alternatively, an extra drying step may be provided in which the agglomerates/spray dried powders/extrudates etc are dried by any convenient means. Suitable examples include drying ovens and fluidised bed dryers. For example, in a drying oven, the detergent matrix powder may be passed through such a drying oven on a conveyor or other  
25 convenient means. Preferably the free moisture in the detergent matrix component will be dried to below 1 wt%, more preferably below 0.5 wt%, or even below 0.1 or 0.05 wt% of the detergent matrix component. There is not necessarily a direct correlation between the free moisture content of the detergent matrix component and the eRH, so the eRH for a particular detergent matrix must be measured in order to ensure the appropriate eRH is  
30 achieved. In a particularly preferred aspect of the invention, the detergent matrix component is over-dried (i.e. at least some of the bound water which is naturally associated with one or more of the chemical constituents of the component is at least

partially removed). Particularly preferred detergent matrix components are spray dried powders.

In accordance with a second aspect of the invention, the inventors have found that in a detergent composition which comprises the effervescence particles, the incorporation of a low density surfactant-containing detergent matrix component surprisingly promotes effervescence of the detergent, and in particular promotes both the initial effervescence and the duration of the effervescence. This can be particularly advantageous as it enables lower amounts of effervescence particle to be used in the detergent compositions of the invention to achieve the same effervescence effect. Thus, a low density detergent matrix component is a preferred ingredient in the low eRH detergent compositions of the invention.

The low density detergent matrix component preferably has a bulk density of at least 100g/l, more preferably at least 120g/l. Preferably the bulk density is below 400g/l or even below 350g/l or 300g/l. The median particle size of the low bulk density detergent matrix component is preferably at least 50  $\mu\text{m}$ , more preferably at least 75 $\mu\text{m}$  and most preferably at least 100 $\mu\text{m}$ . Generally, the median particle size will be below 500 $\mu\text{m}$ , preferably below 450 $\mu\text{m}$  and even below 400 or 350 $\mu\text{m}$ . The low density detergent matrix component is preferably added to the detergent composition in amounts from about 0.1% to 40% by weight.

The small particle size detergent matrix component has a bulk density of from 400 to 800, preferably, from 500 to 700 g/l. The median particle size of the small particle size detergent matrix component is from 50 to 300  $\mu\text{m}$ , preferably from 150 to 250 $\mu\text{m}$ . The small particle size detergent matrix component is preferably added to the detergent composition in amounts from about 0.1% to 10% by weight.

Preferably the surfactant content in the low density detergent matrix component is at least 20 wt%, more preferably at least 25wt% and most preferably at least 30 wt% based on the total weight of the detergent matrix component. Any of the surfactants described below are suitable, preferred are any suds-generating surfactants. Anionic and/or nonionic surfactants are particularly preferred. Cationic surfactants which have good foaming properties may also be preferred. As for the other detergent matrix components described, the low density detergent matrix component preferably comprises additional ingredients which may be fillers such as sulphate or more preferably comprises

additional detergent ingredients as described below. Particularly preferred additional ingredients are alkali metal carbonates, preferably sodium carbonate, silicates which may be either amorphous or crystalline, zeolites, brighteners and polymeric materials such as acrylate polymers which may be either homo or copolymers, for example copolymers of acrylic and maleic acids are particularly preferred.

Preferably the low density detergent matrix component is incorporated into the detergent compositions of the invention in amounts greater than 0.1 wt% based on the total weight of the detergent composition, more preferably in amounts greater than 2 wt% or even greater than 5 wt% or 10 wt%. Generally, the detergent compositions of the invention will contain no more than 20 wt% of the low density detergent matrix component, preferably no more than 15 wt%, or even no more than 10 wt% based on the total weight of detergent composition. Preferably the weight ratio of effervescence components to the low density detergent matrix component is from 10:1 to 1:10, preferably being from 5:1 to 1:3 and most preferably from 3:1 to 1:2.

The low density detergent matrix component can be prepared by any of the methods for making the detergent matrix component as described above as long as they permit a sufficiently low density to be achieved. Spray drying processes and fluid bed agglomeration processes are particularly suitable. Spray drying processes are particularly preferred.

#### Additional Detergent Ingredients

As described above, the detergent matrix may comprise one or more additional detergent ingredients. These may comprise detergent raw materials or may be pre-formed particulates made by processing at least one detergent ingredient with other ingredients which may be active or inactive in the detergent to form a solid particulate. Where the particulate components are detergent raw materials, any particulate detergent ingredient is suitable. These may be solid surfactants or soaps, or water soluble or dispersible polymeric materials, enzymes, bleaching components such as bleach activators or bleach salts such as peroxy salts. Surfactants and additional detergent ingredients are discussed in more detail below. Any of the ingredients listed below may be added to the detergent compositions claimed either as individual solid particulates or as pre-formed particulates or via a detergent matrix component. These additional detergent ingredients may be incorporated into the detergent matrix if needed, having undergone a drying step.

Whether a drying step is needed depends upon the form and level of incorporation of the individual additional ingredient materials and the eRH which they and the detergent matrix component and other ingredients provide in the overall detergent matrix. In accordance with the first embodiment of the invention, the final detergent matrix must

5 have an eRH below 30%.

### Detergent Ingredients

#### Surfactant

Suitable surfactants for use in the invention are anionic, nonionic, ampholytic, and zwitterionic classes of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin

10 and Heuring on December 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

Preferably, the particles and detergent compositions of the present invention comprises an additional anionic surfactant. Essentially any anionic surfactants useful for

15 deterative purposes can be comprised in the detergent composition. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate and sulfonate surfactants are preferred.

20 The anionic surfactants may be present in the detergent matrix component in amounts below 25 wt % or even below 20 wt % but in a final detergent composition comprising the particle, is preferably present at a level of from 0.1% to 60%, more preferably from 1 to 40%, most preferably from 5% to 30% by weight.

Other anionic surfactants include the anionic carboxylate surfactants such as alkyl

25 ethoxy carboxylates, alkyl polyethoxy polycarboxylates and soaps ("alkyl carboxyls") such as water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors. Other suitable anionic surfactants are the alkali metal

30 sarcosinates of formula  $R-CON(R^1)CH_2COOM$ , wherein R is a  $C_5-C_{17}$  linear or branched alkyl or alkenyl group,  $R^1$  is a  $C_1-C_4$  alkyl group and M is an alkali metal ion.



Other anionic surfactants include isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C<sub>12</sub>-C<sub>18</sub> monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C<sub>6</sub>-C<sub>14</sub> diesters), N-acyl

5    sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates,

10    alkyl phenol ethylene oxide ether sulfates, the C<sub>5</sub>-C<sub>17</sub> acyl-N-(C<sub>1</sub>-C<sub>4</sub> alkyl) and -N-(C<sub>1</sub>-C<sub>2</sub> hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein). Alkyl sulfate surfactants are preferably selected from the linear and branched primary C<sub>10</sub>-C<sub>18</sub> alkyl sulfates, more preferably the C<sub>11</sub>-C<sub>15</sub> branched chain alkyl

15    sulfates and the C<sub>12</sub>-C<sub>14</sub> linear chain alkyl sulfates. Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C<sub>10</sub>-C<sub>18</sub> alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C<sub>11</sub>-C<sub>18</sub>, most preferably C<sub>11</sub>-C<sub>15</sub> alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles

20    of ethylene oxide per molecule.

Preferred surfactant combinations are mixtures of the preferred alkyl sulfate and/or sulfonate and alkyl ethoxysulfate surfactants optionally with cationic surfactant. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic sulfonate surfactants suitable for use herein include the salts of C<sub>5</sub>-C<sub>20</sub>

25    linear alkylbenzene sulfonates, alkyl ester sulfonates, C<sub>6</sub>-C<sub>22</sub> primary or secondary alkane sulfonates, C<sub>6</sub>-C<sub>24</sub> olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Essentially any alkoxyated nonionic surfactant or mixture is suitable herein. The

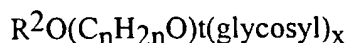
30    ethoxylated and propoxylated nonionic surfactants are preferred.

Preferred alkoxyated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are particularly suitable for use herein. Particularly preferred are the condensation products of straight or branched, primary or secondary alcohols having an alkyl group containing from 6 to 22 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula  $R^2CONR^1Z$  wherein :  $R^1$  is H,  $C_1$ - $C_4$  hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy, or a mixture thereof, preferable  $C_1$ - $C_4$  alkyl; and  $R^2$  is a  $C_5$ - $C_{31}$  hydrocarbyl; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl.

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units. Preferred alkylpolyglycosides have the formula:



wherein  $R^2$  is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl is preferably derived from glucose.

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids. Suitable amine oxides include those compounds having the formula  $R^3(OR^4)_xN^0(R^5)_2$  wherein  $R^3$  is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing

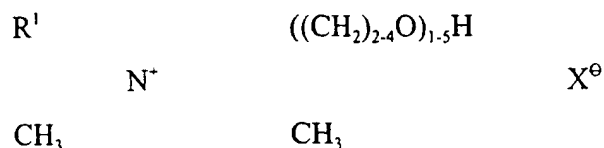
from 8 to 26 carbon atoms;  $R^4$  is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof;  $x$  is from 0 to 5, preferably from 0 to 3; and each  $R^5$  is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are  $C_{10}$ - $C_{18}$  alkyl

5 dimethylamine oxide, and  $C_{10-18}$  acylamido alkyl dimethylamine oxide.

Zwitterionic surfactants can also be incorporated into the detergent compositions in accord with the invention. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium  
10 compounds. Betaines such as  $C_{12-18}$  dimethyl-ammonio hexanoate and the  $C_{10-18}$  acylamidopropane (or ethane) dimethyl (or diethyl) betaines and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Suitable cationic surfactants to be used herein include the quaternary ammonium surfactants. Preferably the quaternary ammonium surfactant is a mono  $C_6$ - $C_{16}$ ,  
15 preferably  $C_6$ - $C_{10}$  N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups. Preferred are also the mono-alkoxylated and bis-alkoxylated amine surfactants.

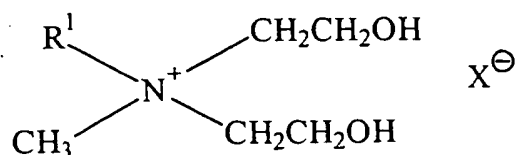
Cationic ester surfactants such as choline ester surfactants, have for example been disclosed in US Patents No.s 4228042, 4239660 and 4260529 are also suitable as are  
20 cationic mono-alkoxylated amine surfactants preferably of the general formula I:



25 wherein  $R^1$  is  $C_{10}$ - $C_{18}$  hydrocarbonyl and mixtures thereof, especially  $C_{10}$ - $C_{14}$  alkyl, preferably  $C_{10}$  and  $C_{12}$  alkyl, and  $X$  is any convenient anion to provide charge balance, preferably chloride or bromide.

The levels of the cationic mono-alkoxylated amine surfactants in the detergent compositions of the invention are generally from 0.1% to 20%, preferably from 0.2% to  
30 7%, most preferably from 0.3% to 3.0% by weight.

Cationic bis-alkoxylated amine surfactant such as



are also useful, wherein R<sup>1</sup> is C<sub>10</sub>-C<sub>18</sub> hydrocarbyl and mixtures thereof, preferably C<sub>10</sub>, C<sub>12</sub>, C<sub>14</sub> alkyl and mixtures thereof. X is any convenient anion to provide charge balance, preferably chloride.

#### Bleach Activator

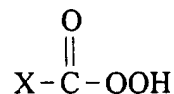
The detergent compositions of the invention preferably comprise a bleach activator, preferably comprising an organic peroxyacid bleach precursor. It may be preferred that the composition comprises at least two peroxy acid bleach precursors, preferably at least one hydrophobic peroxyacid bleach precursor and at least one hydrophilic peroxy acid bleach precursor, as defined herein. The production of the organic peroxyacid occurs then by an in situ reaction of the precursor with a source of hydrogen peroxide. The bleach activator may alternatively, or in addition comprise a preformed peroxy acid bleach. Preferably, the bleach activator is present as a separate, admixed particle.

Preferably, any bleach activator is present in a particulate component having an average particle size, by weight, of from 600 microns to 1400 microns, preferably from 700 microns to 1100 microns. It may be preferred that at least 80%, preferably at least 90% or even at least 95 % or even substantially 100% of the component or components comprising the bleach activator have a particle size of from 300 microns to 1700 microns, preferably from 425 microns to 1400 microns. Preferred hydrophobic peroxy acid bleach precursor preferably comprise a compound having an oxy-benzene sulphonate group, preferably NOBS, DOBS, LOBS and/ or NACA-OBS. Preferred hydrophilic peroxy acid bleach precursors preferably comprises TAED.

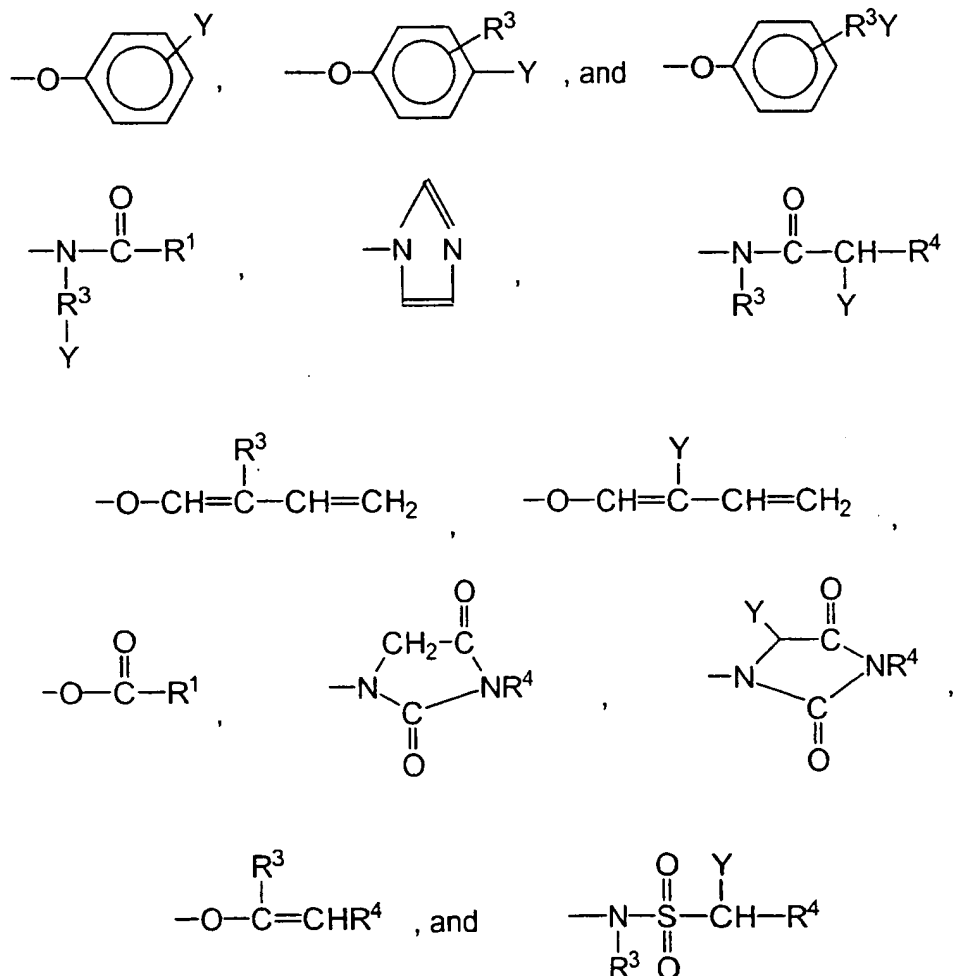
#### Peroxyacid Bleach Precursor

Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as X-C(O)-L where L is a leaving group and X is

essentially any functionality, such that on perhydrolysis the structure of the peroxyacid produced is



- For the purpose of the invention, hydrophobic peroxyacid bleach precursors produce a peroxy acid of the formula above wherein X is a group comprising at least 6 carbon atoms and a hydrophilic peroxyacid bleach precursor produces a peroxyacid bleach of the formula above wherein X is a group comprising 1 to 5 carbon atoms. The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition. Preferred L groups are selected from the group consisting of:



and mixtures thereof, wherein  $R^1$  is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms,  $R^3$  is an alkyl chain containing from 1 to 8 carbon atoms,  $R^4$  is H or  $R^3$ , and Y is H or a solubilizing group. Any of  $R^1$ ,  $R^3$  and  $R^4$  may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups.

The preferred solubilizing groups are  $-\text{SO}_3^- \text{M}^+$ ,  $-\text{CO}_2^- \text{M}^+$ ,  $-\text{SO}_4^- \text{M}^+$ ,  $-\text{N}^+(\text{R}^3)_4 \text{X}^-$  and  $\text{O}=\text{N}(\text{R}^3)_3$  and most preferably  $-\text{SO}_3^- \text{M}^+$  and  $-\text{CO}_2^- \text{M}^+$  wherein  $R^3$  is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator.

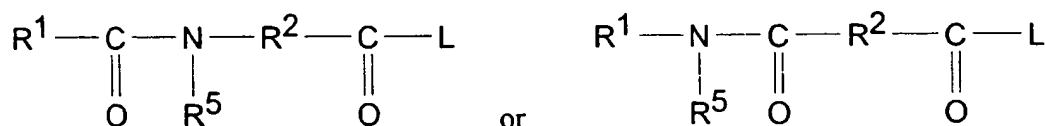
Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

Peroxyacid bleach precursor compounds are preferably incorporated in final detergent compositions at a level of from 0.5% to 30% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight. The ratio of hydrophilic to hydrophobic bleach precursors, when present, is preferably from 10:1 to 1:10, more preferably from 5:1 to 1:5 or even from 3:1 to 1:3. Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis. Preferred alkyl percarboxylic precursor compounds of the imide type include the N-, N,N<sup>1</sup>N<sup>1</sup> tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred as hydrophilic peroxy acid bleach precursor. Other preferred alkyl percarboxylic acid

precursors include sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose.

- Amide substituted alkyl peroxyacid precursor compounds are suitable herein,  
 5 including those of the following general formulae:



- wherein  $\text{R}^1$  is an aryl or alkaryl group with from about 1 to about 14 carbon atoms,  $\text{R}^2$  is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and  $\text{R}^5$  is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can  
 10 be essentially any leaving group.  $\text{R}^1$  preferably contains from about 6 to 12 carbon atoms.  $\text{R}^2$  preferably contains from about 4 to 8 carbon atoms.  $\text{R}^1$  may be straight chain or branched alkyl, substituted aryl or alkaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for  $\text{R}^2$ .  $\text{R}^2$  can  
 15 include alkyl, aryl, wherein said  $\text{R}^2$  may also contain halogen, nitrogen, sulphur and other typical substituent groups or organic compounds.  $\text{R}^5$  is preferably H or methyl.  $\text{R}^1$  and  $\text{R}^5$  should not contain more than 18 carbon atoms total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386. It can be preferred that  $\text{R}^1$  and  $\text{R}^5$  forms together with the nitrogen and carbon atom a ring structure.

- 20 Preferred examples of bleach precursors of this type include amide substituted peroxyacid precursor compounds selected from (6-octanamido-caproyl)oxybenzenesulfonate, (6-decanamido-caproyl) oxybenzene- sulfonate, and the highly preferred (6-nonanamidocaproyl)oxy benzene sulfonate, and mixtures thereof as described in EP-A-0170386.

- 25 Perbenzoic acid precursor compounds which provide perbenzoic acid on perhydrolysis benzoxazin organic peroxyacid precursors, as disclosed for example in EP-A-332294 and EP-A-482807 and cationic peroxyacid precursor compounds which produce cationic peroxyacids on perhydrolysis are also suitable.

Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332. Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 5 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides. Preferred cationic peroxyacid 10 precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams and the trialkyl ammonium methylene alkyl caprolactams.

The particles or compositions of the present invention may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed organic peroxyacid, typically at a level of from 0.1% to 15% by weight, more preferably 15 from 1% to 10% by weight. A preferred class of organic peroxyacid compounds are the amide substituted compounds as described in EP-A-0170386. Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioic acid, diperoxytetradecanedioic acid and diperoxyhexadecanedioic acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid are also 20 suitable herein.

#### Peroxide Source

Inorganic perhydrate salts are a preferred source of peroxide. Preferably these salts are present at a level of from 0.01% to 50% by weight, more preferably of from 0.5% to 30% by weight of the composition.

25 Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. Generally these materials are prepared by crystallisation or fluidised bed processes. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred 30 executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product. Suitable coatings comprise inorganic salts such as alkali metal silicate, carbonate or borate salts or



mixtures thereof, or organic materials such as waxes, oils, or fatty soaps. Sodium perborate is a preferred perhydrate salt and can be in the form of the monohydrate of nominal formula  $\text{NaBO}_2\text{H}_2\text{O}_2$  or the tetrahydrate  $\text{NaBO}_2\text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ . Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates herein. Sodium percarbonate is an addition compound having a formula corresponding to  $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ , and is available commercially as a crystalline solid. Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

### Chelants

As used herein, chelants refers to detergent ingredients which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper. Chelants are generally present in the detergent matrix component and/or as dry added additional detergent ingredients so that they are present in the final detergent composition at total levels of from 0.005% to 10%, preferably from 0.1% to 5%, more preferably from 0.25% to 7.5% and most preferably from 0.3% to 2% by weight of the compositions or component

Suitable chelants include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates, preferably, diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate, 1,1 hydroxyethane diphosphonic acid and 1,1 hydroxyethane dimethylene phosphonic acid.

Other suitable chelants for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutamic acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof, and iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The  $\beta$ -alanine-N,N'-diacetic acid, aspartic acid-N,N'-

diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable. EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant.

- 5 Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N,N'-diglutamic acid (EDDG) and 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS) are also suitable. Especially preferred are diethylenetriamine pentacetic acid, ethylenediamine-N,N'-disuccinic acid (EDDS) and 1,1 hydroxyethane diphosphonic acid or the alkali
- 10 metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. In particular the chelating agents comprising an amino or amine group can be bleach-sensitive and are suitable in the compositions of the invention.

#### Water-Soluble Builder Compound

- The detergent compositions herein preferably contain a water-soluble builder
- 15 compound, typically present in the detergent compositions at a level of from 1% to 80% by weight, preferably from 10% to 60%, most preferably from 15% to 40% by weight.

- One preferred detergent composition of the invention comprises phosphate-containing builder material, preferably present at a level of from 0.5% to 60%, more preferably from 5% to 50%, more preferably from 8% to 40% by weight. Suitable
- 20 examples of water-soluble phosphate builders are the alkali metal triphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid. The phosphate-containing builder material preferably comprises
- 25 tetrasodium pyrophosphate or even more preferably anhydrous sodium triphosphate.

- Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, borates, and mixtures of
- 30 any of the foregoing. The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance. Suitable carboxylates containing one carboxy group

include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates or their acids containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447. The most preferred polycarboxylic acid containing three carboxy groups is citric acid, preferably present at a level of from 0.1% to 15%, more preferably from 0.5% to 8% by weight.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred polycarboxylates are hydroxy-carboxylates containing up to three carboxy groups per molecule, particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components. Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders herein.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 1000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 2000 to 100,000.

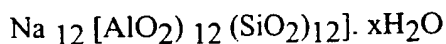
especially 40,000 to 80,000. The polyamino compounds are also useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

#### Partially Soluble or Insoluble Builder Compound

5           The compositions of the invention may contain a partially soluble or insoluble builder compound present in the detergent matrix component and/or the optional additional ingredients. Where present, typically they will be present in the detergent compositions in a total amount of from 0.5% to 60% by weight, preferably from 5% to 50% by weight, most preferably from 8% to 40% weight. Examples of largely water  
10   insoluble builders include the sodium aluminosilicates. As mentioned above, it may be preferred in one embodiment of the invention, that only small amounts of aluminosilicate builder are present.

Suitable aluminosilicate zeolites have the unit cell formula  $\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$  wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at  
15   least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange  
20   materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula:



wherein x is from 20 to 30, especially 27. Zeolite X has the formula  $\text{Na}_{86} [(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 276 \text{H}_2\text{O}$ .

25           Another preferred aluminosilicate zeolite is zeolite MAP builder. The zeolite MAP may be present in amounts from 1 to 80%, more preferably from 15 to 40 wt%. Zeolite MAP is described in EP 384070A (Unilever). It is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, preferably within the range from 0.9 to 1.33 and more  
30   preferably within the range of from 0.9 to 1.2. Of particular interest is zeolite MAP having a silicon to aluminium ratio not greater than 1.15 and, more

particularly, not greater than 1.07. In a preferred aspect the zeolite MAP detergent builder has a particle size, expressed as a median particle size  $d_{50}$  value of from 1.0 to 10.0 micrometres, more preferably from 2.0 to 7.0 micrometres, most preferably from 2.5 to 5.0 micrometres. The  $d_{50}$  value indicates that 50% by weight of the particles have a diameter smaller than that figure. The particle size may, in particular be determined by conventional analytical techniques such as microscopic determination using a scanning electron microscope or by means of a laser granulometer, described herein. Other methods of establishing  $d_{50}$  values are disclosed in EP 384070A.

10 Dyes, Perfumes, Enzymes, Optical Brighteners

A preferred ingredient of the compositions herein are dyes and dyed particles or speckles, which can be bleach-sensitive. The dye as used herein can be a dye stuff or an aqueous or nonaqueous solution of a dye stuff. It may be preferred that the dye is an aqueous solution comprising a dyestuff, at any level to obtain suitable dyeing of the detergent particles or speckles, preferably such that levels of dye solution are obtained up to 2% by weight of the dyed particle, or more preferably up to 0.5% by weight, as described above. The dye may also be mixed with a non-aqueous carrier material, such as non-aqueous liquid materials including nonionic surfactants. Optionally, the dye also comprising other ingredients such as organic binder materials, which may also be a non-aqueous liquid. The dyestuff can be any suitable dyestuff. Specific examples of suitable dyestuffs include E104 - food yellow 13 (quinoline yellow), E110 - food yellow 3 (sunset yellow FCF), E131 - food blue 5 (patent blue V), Ultra Marine blue (trade name), E133 - food blue 2 (brilliant blue FCF), E140 - natural green 3 (chlorophyll and chlorophyllins), E141 and Pigment green 7 (chlorinated Cu phthalocyanine). Preferred dyestuffs may be Monastral Blue BV paste (trade name) and/ or Pigmasol Green (trade name).

Another preferred ingredient of the compositions of the invention is a perfume or perfume composition. Any perfume composition can be used herein. The perfumes may also be encapsulated. Preferred perfumes containing at least one component with a low molecular weight volatile component, e.g. having a molecular weight of from 150 to 450 or preferably 350. Preferably, the perfume component comprises an oxygen-containing

functional group. Preferred functional groups are aldehyde, ketone, alcohol or ether functional groups or mixtures thereof.

Another highly preferred ingredient useful in the particles or compositions herein is one or more additional enzymes. Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, cellulases, endolases, esterases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition. Preferred amylases include, for example,  $\alpha$ -amylases described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl, Duramyl and BAN by Novo Industries A/S. Highly preferred amylase enzymes maybe those described in PCT/US 9703635, and in WO95/26397 and WO96/23873. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight. Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight. The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272. Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from

Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Huge-Jensen et al, issued March 7, 1989.

The compositions herein also preferably contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners, as mentioned above. Examples  
5 are Tinopal-UNPA-GX™ and Tinopal-CBS-X™ by Ciba-Geigy Corporation. Others include Tinopal 5BM-GX™, Tinopal-DMS-X™ and Tinopal AMS-GX™ by Ciba Geigy Corporation.

#### Photo-Bleaching Agent

Photo-bleaching agents are preferred ingredients of the compositions or components  
10 herein. Preferred photo-bleaching agent herein comprise a compounds having a porphin or porphyrin structure. Porphin and porphyrin, in the literature, are used as synonyms, but conventionally porphin stands for the simplest porphyrin without any substituents; wherein porphyrin is a sub-class of porphin. The references to porphin in this application will include porphyrin. The porphin structures preferably comprise a metal element or  
15 cation, preferably Ca, Mg, P, Ti, Cr, Zr, In, Sn or Hf, more preferably Ge, Si or Ga, or more preferably Al, most preferably Zn. It can be preferred that the photo-bleaching compound or component is substituted with substituents selected from alkyl groups such as methyl, ethyl, propyl, t-butyl group and aromatic ring systems such as pyridyl, pyridyl-N-oxide, phenyl, naphthyl and anthracyl moieties. The photo-bleaching compound or  
20 component can have solubilizing groups as substituents. Alternatively, or in addition hereto the photo-bleaching agent can comprise a polymeric component capable of solubilizing the photo-bleaching compound, for example PVP, PVNP, PVI or co-polymers thereof or mixtures thereof. Highly preferred photo-bleaching compounds are compounds having a phthalo-cyanine structure, which preferably have the metal elements  
25 or cations described above.

The phthalocyanines can be substituted for example the phthalocyanine structures which are substituted at one or more of the 1-4, 6, 8-11, 13, 15-18, 20, 22-25, 27 atom positions.

#### Organic Polymeric Ingredients

Organic polymeric compounds are preferred additional herein and are preferably  
30 present as components of any particulate component such as the detergent matrix component where they may act as binders. By organic polymeric compound it is meant herein essentially any polymeric organic compound commonly used as dispersants, and

anti-redeposition and soil suspension agents in detergent compositions, including any of the high molecular weight organic polymeric compounds described as clay flocculating agents herein, including quaternised ethoxylated (poly) amine clay-soil removal/ anti-redeposition agent in accord with the invention. Organic polymeric compound is

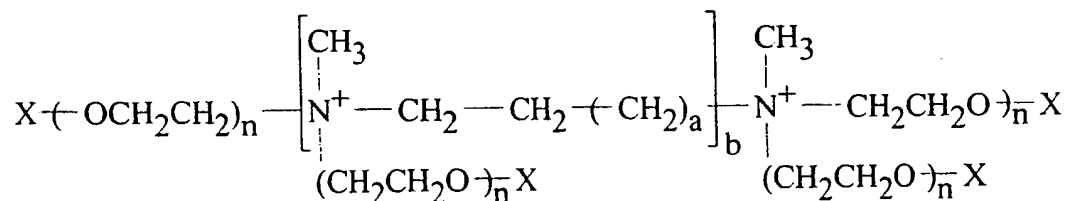
5 typically incorporated in the detergent compositions of the invention at a level of from 0.01% to 30%, preferably from 0.1% to 15%, most preferably from 0.5% to 10% by weight of the compositions or component. Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable

10 herein. Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and

15 most preferably about 4000. Highly preferred polymeric components herein are cotton and non-cotton soil release polymer according to U.S. Patent 4,968,451, Scheibel et al., and U.S. Patent 5,415,807, Gosselink et al., and in particular according to US application no.60/051517. Another organic compound, which is a preferred clay dispersant/ anti-redeposition agent, for use herein, can be the ethoxylated cationic monoamines and

20 diamines of the formula:



wherein X is a nonionic group selected from the group consisting of H, C<sub>1</sub>-C<sub>4</sub> alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof, a is from 0 to 20, preferably

25 from 0 to 4 (e.g. ethylene, propylene, hexamethylene) b is 1 or 0; for cationic monoamines (b=0), n is at least 16, with a typical range of from 20 to 35; for cationic diamines (b=1), n is at least about 12 with a typical range of from about 12 to about 42.



Other dispersants/ anti-redeposition agents for use herein are described in EP-B-011965 and US 4,659,802 and US 4,664,848.

Polymeric dye transfer inhibiting agents when present are generally in amounts from 0.01% to 10 %, preferably from 0.05% to 0.5% and are preferably selected from  
5 polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof, whereby these polymers can be cross-linked polymers.

Polymeric soil release agents, hereinafter "SRA", can optionally be employed in the present components or compositions. If utilized, SRAs will generally be used in amounts  
10 from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight. Preferred SRA's typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles, thereby serving as an anchor for the hydrophilic segments. This can  
15 enable stains occurring subsequent to treatment with the SRA to be more easily cleaned in later washing procedures. Preferred SRA's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through  
20 one, two, three, four or more positions, without, of course, forming a densely crosslinked overall structure.

Suitable SRAs are for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Other SRAs include the nonionic end-capped 1,2-propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987  
25 to Gosselink et al. Other examples of SRA's include: the partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al. SRAs also include: simple  
30 copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as

the hydroxyether cellulosic polymers available as METHOCEL from Dow; the C<sub>1</sub>-C<sub>4</sub> alkyl celluloses and C<sub>4</sub> hydroxyalkyl celluloses, see U.S. 4,000,093, December 28, 1976 to Nicol, et al.; and the methyl cellulose ethers having an average degree of substitution (methyl) per anhydroglucose unit from about 1.6 to about 2.3 and a solution viscosity of  
5 from about 80 to about 120 centipoise measured at 20°C as a 2% aqueous solution. Such materials are available as METOLOSE SM100 and METOLOSE SM200, which are the trade names of methyl cellulose ethers manufactured by Shin-etsu Kagaku Kogyo KK.

Additional classes of SRAs include those described in U.S. 4,201,824, Violland et al. and U.S. 4,240,918 Lagasse et al.; U.S. 4,525,524 Tung et al., and U.S. 4,201,824,  
10 Violland et al.

#### Suds Suppressing System

The detergent compositions herein, in particular when formulated for use in machine washing compositions, may comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.02% to 10%, most preferably from 0.05%  
15 to 3% by weight of the composition or component. Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds and 2-alkyl alcanol antifoam compounds or soap. By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent  
20 composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety  
25 of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units. Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof as described in US Patent 2,954,347, issued September 27, 1960 to Wayne St.  
30 John. Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols,

aliphatic C<sub>18</sub>-C<sub>40</sub> ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyl diamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

A preferred suds suppressing system comprises antifoam compound, preferably comprising in combination polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10% such as DCO544, commercially available from DOW Corning, and an inert carrier fluid compound, most preferably comprising a C<sub>16</sub>-C<sub>18</sub> ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of 5 to 80%, preferably 10 to 70% by weight.

A highly preferred particulate suds suppressing system is described in EP-A-0210731. EP-A-0210721 discloses other preferred particulate suds suppressing systems. Other highly preferred suds suppressing systems comprise polydimethylsiloxane or mixtures of silicone, such as polydimethylsiloxane, aluminosilicate and polycarboxylic polymers, such as copolymers of laic and acrylic acid.

Other optional ingredients suitable for inclusion in the compositions of the invention include colours and filler salts, with sodium sulfate being a preferred filler salt.

Highly preferred compositions contain from about 2% to about 10% by weight of an organic acid, preferably citric acid. Also, preferably combined with a carbonate salt, minor amounts (e.g., less than about 20% by weight) of neutralizing agents, buffering agents, phase regulants, hydrotropes, enzyme stabilizing agents, polyacids, suds regulants, opacifiers, anti-oxidants, bactericides and dyes, such as those described in US Patent 4,285,841 to Barrat et al., issued August 25, 1981 (herein incorporated by reference), can be present.

The detergent compositions can include as an additional component a chlorine-based bleach. However, since the detergent compositions of the invention are solid, most liquid chlorine-based bleaching will not be suitable for these detergent compositions and only granular or powder chlorine-based bleaches will be suitable. Alternatively, a chlorine based bleach can be added to the detergent composition by the user at the beginning or during the washing process. The chlorine-based bleach is such that a hypochlorite species is formed in aqueous solution. The hypochlorite ion is chemically represented by the formula  $\text{OCI}^-$ . Those bleaching agents which yield a hypochlorite species in aqueous solution include alkali metal and alkaline earth metal hypochlorites, hypochlorite addition products, chloramines, chlorimines, chloramides, and chlorimides. Specific examples include sodium hypochlorite, potassium hypochlorite, monobasic calcium hypochlorite, dibasic magnesium hypochlorite, chlorinated trisodium phosphate dodecahydrate, potassium dichloroisocyanurate, sodium dichloroisocyanurate sodium dichloroisocyanurate dihydrate, trichlorocyanuric acid, 1,3-dichloro-5,5-dimethylhydantoin, N-chlorosulfamide, Chloramine T, Dichloramine T, chloramine B and Dichloramine B. A preferred bleaching agent for use in the compositions of the instant invention is sodium hypochlorite, potassium hypochlorite, or a mixture thereof. A preferred chlorine-based bleach can be Triclosan (trade name).

Most of the above-described hypochlorite-yielding bleaching agents are available in solid or concentrated form and are dissolved in water during preparation of the compositions of the instant invention. Some of the above materials are available as aqueous solutions.

#### Laundry Washing Method

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accord with the invention. By an effective amount of the detergent composition it is meant from 10g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods. Preferred washing machines may be the so-called low-fill machines.

In a preferred use aspect the composition is formulated such that it is suitable for hard-surface cleaning or hand washing. In another preferred aspect the detergent composition is a pre-treatment or soaking composition, to be used to pre-treat or soak soiled and stained fabrics.

5

### EXAMPLES

The following examples are presented for illustrative purposes only and are not to be construed as limiting the scope of the appended claims in any way.

#### 10 *Abbreviations used in the Examples*

In the detergent compositions, the abbreviated component identifications have the following meanings:

	LAS	: Sodium linear C11-13 alkyl benzene sulfonate
	TAS	:Sodium tallow alkyl sulfate
15	CxyAS	:Sodium C1x - C1y alkyl sulfate
	Branched AS	:branched sodium alkyl sulfate as described in WO99/19454
	C46SAS	:Sodium C14 - C16 secondary (2,3) alkyl sulfate
	CxyEzS	:Sodium C1x-C1y alkyl sulfate condensed with z moles of ethylene oxide
	CxyEz	:C1x-C1y predominantly linear primary alcohol condensed with an
20		average of z moles of ethylene oxide
	QAS	: R <sub>2</sub> .N+(CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH) with R <sub>2</sub> = C12 - C14
	QAS 1	:R <sub>2</sub> .N+(CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH) with R <sub>2</sub> = C8 - C11
	APA	:C8 - C10 amido propyl dimethyl amine
	Soap	:Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow
25		and coconut fatty acids
	STS	:Sodium toluene sulphonate
	CFAA	:C12-C14 (coco) alkyl N-methyl glucamide
	TFAA	:C16-C18 alkyl N-methyl glucamide
	TPKFA	:C12-C14 topped whole cut fatty acids
30	STPP	:Anhydrous sodium tripolyphosphate
	TSPP	:Tetrasodium pyrophosphate

- Zeolite A :Hydrated sodium aluminosilicate of formula  $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$  having a primary particle size in the range from 0.1 to 10 micrometers (weight expressed on an anhydrous basis)
- NaSKS-6 :Crystalline layered silicate of formula d-  $\text{Na}_2\text{Si}_2\text{O}_5$
- 5 Citric acid :Anhydrous citric acid
- Borate :Sodium borate
- Carbonate :Anydrous sodium carbonate: particle size 200 $\mu\text{m}$  to 900 $\mu\text{m}$
- Bicarbonate :Anhydrous sodium bicarbonate with a particle size distribution between 400 $\mu\text{m}$  and 1200 $\mu\text{m}$
- 10 Silicate :Amorphous sodium silicate ( $\text{SiO}_2:\text{Na}_2\text{O} = 2.0:1$ )
- Sulfate :Anhydrous sodium sulfate
- Mg sulfate :Anhydrous magnesium sulfate
- Citrate :Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425 $\mu\text{m}$  and 850 $\mu\text{m}$
- 15 MA/AA :Copolymer of 1:4 maleic/acrylic acid, average m. wt. about 70,000
- MA/AA (1) :Copolymer of 4:6 maleic/acrylic acid, average m. wt. about 10,000
- AA :Sodium polyacrylate polymer of average molecular weight 4,500
- CMC :Sodium carboxymethyl cellulose
- Cellulose ether:Methyl cellulose ether with a degree of polymerization of 650 available
- 20 from Shin Etsu Chemicals
- Protease :Proteolytic enzyme, having 3.3% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Savinase
- Protease I :Proteolytic enzyme, having 4% by weight of active enzyme, as described in WO 95/10591, sold by Genencor Int. Inc.
- 25 Alcalase :Proteolytic enzyme, having 5.3% by weight of active enzyme, sold by NOVO Industries A/S
- Cellulase :Cellulytic enzyme, having 0.23% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Carezyme
- Amylase :Amylolytic enzyme, having 1.6% by weight of active enzyme, sold by
- 30 NOVO Industries A/S under the tradename Termamyl 120T
- Lipase :Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase

- Lipase (1) :Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase Ultra
- Endolase :Endoglucanase enzyme, having 1.5% by weight of active enzyme, sold by NOVO Industries A/S
- 5 PB4 :Sodium perborate tetrahydrate of nominal formula  $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$
- PB1 :Anhydrous sodium perborate bleach of nominal formula  $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
- Percarbonate :Sodium percarbonate of nominal formula  $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
- 10 NOBS :Nonanoyloxybenzene sulfonate in the form of the sodium salt
- NAC-OBS :(6-nonamidocaproyl) oxybenzene sulfonate
- TAED :Tetraacetylenethylenediamine
- DTPA :Diethylene triamine pentaacetic acid
- DTPMP :Diethylene triamine penta (methylene phosphonate), marketed by
- 15 Monsanto under the Tradename Dequest 2060
- EDDS :Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer sodium salt.
- Photoactivated bleach :Sulfonated zinc phthalocyanine encapsulated in bleach (1) dextrin- sol.pol.
- Photoactivated bleach
- 20 bleach :Sulfonated alumino phthalocyanine encapsulated in bleach (2) dextrin soluble polymer
- Brightener 1 :Disodium 4,4'-bis(2-sulphostyryl)biphenyl
- Brightener 2 :Disodium 4,4'-bis(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino stilbene-2,2'-disulfonate
- 25 HEDP :1,1-hydroxyethane diphosphonic acid
- PEGx :Polyethylene glycol, with a molecular weight of x (typically 4,000)
- PEO :Polyethylene oxide, with an average molecular weight of 50,000
- TEPAE :Tetraethylenepentaamine ethoxylate
- PVI :Polyvinyl imidosole, with an average molecular weight of 20,000
- 30 PVP :Polyvinylpyrrolidone polymer, with an average m. wt. of 60,000
- PVNO :Polyvinylpyridine N-oxide polymer, with an av. m. wt. of 50,000
- PVPVI :Copol of polyvinylpyrrolidone and vinylimidazole (av. m wt of 20,000)

- QEA :bis((C<sub>2</sub>H<sub>5</sub>O)(C<sub>2</sub>H<sub>4</sub>O)<sub>n</sub>)(CH<sub>3</sub>)-N<sup>+</sup>-C<sub>6</sub>H<sub>12</sub>-N<sup>+</sup>-(CH<sub>3</sub>) bis((C<sub>2</sub>H<sub>5</sub>O)-(C<sub>2</sub>H<sub>4</sub> O))<sub>n</sub>, wherein n = from 20 to 30
- SRP 1 :Anionically end capped poly esters
- SRP 2 :Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
- 5 PEI :Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per nitrogen
- Silicone
- antifoam :Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1
- 10 Opacifier :Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621
- Wax :Paraffin wax
- HMEO :Hexamethylenediamine tetra(ethylene oxide)<sub>24</sub>

15 Example 1: Preparation of Effervescence Particle

- A 2 kg batch of citric acid and sodium carbonate having a composition of 64wt% citric acid/36 wt% sodium carbonate was prepared by mixing in a Hosokawa Mikron 'Nautamix' DBY-5R rotating screw mixer for five minutes at a speed setting of 9(maximum): 1280 g anhydrous citric acid ex Citrique Belge (Fine Granular Grade: 20 16/40) having a particle size of from 200-400µm and 720g anhydrous Sodium Carbonate(Light Soda Ash ex Brunner Mond) pre-milled using a Hosokawa Mikron Air-Classifying Mill(ACM 15) to a median particle size of 5µm. The mixture was then compacted in a Bepex Compaction Unit (Roll 200mm Diameter, 50mm Width): the pre-mixed powders were poured into the feed-hopper above the compacting rolls. The feed-hopper has a vertical screw which feeds the powder into the rolls. The force applied to 25 push these two rolls together known as compaction force was adjusted to 80kN by adjusting the feed-screw speed. The compacted material was collected in the form of broken and unbroken corrugated sheets which were then milled in a Hosokawa Bepex F200 Flake Breaker at speed setting 1. This equipment consists of a Rolling Cage with a 30 1000µm Screen.

The material produced by the Flake breaker was then placed on a Vibrating Sieving device( Retsch model AST200) with sieve size of 355µm. The material retained



on the screen was the desired finished particle (effervescence particle A in the table below) with median particle size 620 $\mu$ m, and the fines were removed for recycle.

The process is repeated using the following mixtures of components in the quantities (respective amounts are given in wt% based on the effervescence particle)  
5 given in table 1, to make alternative effervescence particles B-E.

Table 1

Effervescence Particle	B	C	D	E
Citric acid	40	10	55	-
Malic acid	20	30	-	35
Tartaric acid	-	-	-	15
Sodium carbonate	25	70	-	40
Sodium bicarbonate	15	-	45	10

These effervescence particles are then incorporated into detergent compositions as set out in Examples 2 to 6.

Example 2

A spray dried granule, having the composition set out in example 3 below, produced by forming an aqueous slurry which is then formed into particulates in a spray-drying tower is then mixed with, 5 wt% TAED, 1 wt% suds suppressor, 7.5 wt% sodium carbonate and 2.5 wt% sodium sulphate, as additional detergent ingredients in an Eirich mixer. An aqueous solution of PEG-4000 (35% by weight solids) is then sprayed onto the mixture, which is allowed to granulate for 5 minutes. The resultant product is screened to collect particles between 300 and 1200 microns. 10 wt% sodium percarbonate, 0.5 wt% perfume and 1 wt% enzymes (comprising a mixture of prills comprising amylase, cellulase, protease and lipase) are then dry added and mixed. The mixture produced has an eRH of 59%. 10 wt% effervescence particles of any of formulations A to E or mixtures of these are then added to this mixture in a Nautamix conical mixer and subsequently packed into detergent cartons.

Example 3

A spray dried granule is produced on a counter-current spray drying tower with an air inlet temperature of 300°C. Agglomerates and other admixes (see Table 2) are mixed

with the spray dried granule in a batch rotating drum mixer. The detergent matrix has an eRH of 38%. The effervescence particle A is then added, and the product is then packed into detergent cartons. Further examples of detergent compositions according to the invention may be prepared by the use of effervescence particles B to E or mixtures of any of the particles A to E.

Table 2

<u>Spray dried Granule</u>		<u>50%</u>
	Spray dried granule composition	% Weight of Total
10	Feed	
	LAS	10.4
	Tallow Alkyl Sulphate	1.6
	EDDS	0.4
	Brightener 15	0.1
15	Magnesium sulphate	0.7
	Sokalan CP5	2.5
	HEDP	0.3
	Sodium carbonate	8.4
	Sodium sulphate	23.5
20	Zeolite A	40.0
	Misc. (water, perfume, etc.)	<u>12.07</u>
		100.0
<u>Anionic surfactant agglomerate</u>		<u>10%</u>
	Agglomerate composition	% Weight of Total Feed
25	C <sub>45</sub> alkyl ethoxylate sulfate (EO 0.6)	29.1
	Zeolite A	45.0
	Sodium carbonate	15.1
	Polyethylene glycol (MW 4000)	1.3
	Misc. (water, perfume, etc.)	<u>9.5</u>
30		
		100.0
<u>Percarbonate</u>		<u>10%</u>

<u>TAED</u>	<u>5%</u>
<u>Effervescence granule</u>	<u>10%</u>
<u>Minors</u>	<u>15%</u>

5    Example 4

Example 3 is repeated except that the spray dried granule is dried at the higher tower inlet temperature of 350°C and some of the bound moisture is removed. In this case the detergent matrix eRH was 24%.

Example 5

- 10    The detergent matrix of example 3 is reproduced and to it is added 5% of overdried zeolite in a Nautamix conical mixer. (Overdried zeolite is a Zeolite A which has had more than half of the water of crystallisation removed by additional drying). The resulting detergent matrix has an eRH of 12%. 10% of effervescence particle B is then added to this matrix and the product packed into detergent cartons. Alternative examples can be
- 15    prepared by the use of any of effervescence particles B to E or mixtures of any of particles A to E.

Example 6

- Spray dried particles, agglomerates and builder agglomerates of the formulation described in Tables 3A and 3B below are fed first into a Lodige KM™ 600 mixer at 660
- 20    kg, with the drum rotation at 100 RPM and cutter speed at 3600RPM. The resulting mixture is fed into a fluid bed dryer. Optionally an aqueous solution of PEG-4000 (30% by weight solids) is sprayed onto the mixture in the first of three stages in the fluid bed dryer. The resulting product is screened to collect the particles in the range of about 600 to about 1100μ. The fines are recycled to the Lodige KM and the large particles are
- 25    ground and recycled to the fluid bed dryer. The dry-add detergent components and spray-on from the tables below are then added. The detergent matrix eRH was typically around 14%.

**TABLE 3 A**

The following compositions are in accordance with the invention.

	A	B	C	D	E	F	G	H	I
<u>Spray-dried Granules</u>									
LAS	10.0	10.0	15.0	5.0	8.0	10.0	-	-	-
TAS	-	1.0	-				-	-	-
MBAS	-	-		5.0	8.0		-	-	-
C <sub>45</sub> AS	-	-	1.0		1.0	2.0	-	-	-
C <sub>45</sub> AE <sub>3</sub> S	-	-		1.0			-	-	-
QAS			1.0	1.0			-	-	-
DTPA, HEDP and/or EDDS	0.3	0.3	0.5	0.3			-	-	-
MgSO <sub>4</sub>	0.5	0.5	0.1	-			-	-	-
Sodium citrate	-	-	-	3.0	5.0		-	-	-
Sodium carbonate	10.0	7.0	15.0		10.0	10.0	-	-	-
Sodium sulphate	5.0	5.0	-	-	5.0	3.0	-	-	-
Sodium silicate 1.6R	-	-	-	-	2.0		-	-	-
Zeolite A	16.0	18.0	20.0	20.0	-	-	-	-	-
SKS-6	-	-	-	3.0	5.0	-	-	-	-
MA/AA or AA	1.0	2.0	11.0	-	-	2.0	-	-	-
PEG 4000	-	2.0	-	1.0	-	1.0	-	-	-
QEA	1.0	-	-	-	1.0	-	-	-	-
Brightener	0.05	0.05	0.05	-	0.05	-	-	-	-
Silicone oil	0.01	0.01	0.01	-	-	0.01	-	-	-
Bulk density of spray dried granule (g/l)	300	250	190	320	350	200	-	-	-
<u>Agglomerate</u>									
LAS			-	-	-	-	2.0	2.0	-
MBAS			-	-	-	-	-	-	1.0
C <sub>45</sub> AS			-	-	-	-	2.0	-	-
AE <sub>3</sub>			-	-	-	-	-	1.0	0.5
Carbonate			-	-	-	1.0	1.0	1.0	-

Sodium citrate			-	-	-	-	-	-	5.0
CFAA			-	-	-	-	-	-	-
Citric acid			-	-	-	4.0	-	1.0	1.0
QEA			-	-	-	2.0	2.0	1.0	-
SRP			-	-	-	1.0	1.0	0.2	-
Zeolite A			-	-	-	15.0	26.0	15.0	16.0
Sodium silicate			-	-	-	-	-	-	-
PEG	-	-	-	-	-	-	4.0	-	-
<u>Builder Agglomerates</u>									
SKS-6	6.0	-	-	-	6.0	3.0	-	7.0	10.0
LAS	4.0	5.0	-	-	5.0	3.0	-	10.0	12.0
<u>Dry-add particulate components</u>									
Effervescence Particle A	8.0	10.0			12.0			2.0	4.0
Effervescence Particle B			10.0						
Effervescence Particle C				4.0					
Effervescence Particle D						8.0			
Effervescence Particle E							2.0		
QEA	-	-	-	0.2	0.5	-	-	-	-
NACAOBS	3.0	-	-	1.5	-	-	-	2.5	-
NOBS	-	3.0	3.0	-	-	-	-	-	5.0
TAED	2.5	-	-	1.5	2.5	6.5	-	1.5	-
MBAS	-	-	-	8.0	-	-	8.0	-	4.0



LAS	10.0	10.0	16.0	5.0	5.0	10.0	-	-	-
TAS	-	1.0	-	-	-	-	-	-	-
MBAS	-	-	-	5.0	5.0	-	-	-	-
C <sub>45</sub> AS	-	-	1.0	-	2.0	2.0	-	-	-
C <sub>45</sub> AE <sub>3</sub> S	-	-	-	1.0	-	-	-	-	-
QAS	-	-	1.0	1.0	-	-	-	-	-
DTPA, HEDP and/or EDDS	0.3	0.3	0.3	0.3	-	-	-	-	-
MgSO <sub>4</sub>	0.5	0.4	0.1	-	-	-	-	-	-
Sodium citrate	10.0	12.0	17.0	3.0	5.0	-	-	-	-
Sodium carbonate	15.0	8.0	15.0	-	-	10.0	-	-	-
Sodium sulphate	5.0	5.0	-	-	5.0	3.0	-	-	-
Sodium silicate 1.6R	-	-	-	-	2.0	-	-	-	-
Zeolite A	-	-	-	2.0	-	-	-	-	-
SKS-6	-	-	-	3.0	5.0	-	-	-	-
MA/AA or AA	1.0	2.0	10.0	-	-	2.0	-	-	-
PEG 4000	-	2.0	-	1.0	-	1.0	-	-	-
QEA	1.0	-	-	-	1.0	-	-	-	-
Brightener	0.05	0.05	0.05	-	0.05	-	-	-	-
Silicone oil	0.01	0.01	0.01	-	-	0.01	-	-	-
<u>Agglomerate</u>									
LAS	-	-	-	-	-	-	2.0	2.0	-
MBAS	-	-	-	-	-	-	-	-	1.0
C <sub>45</sub> AS	-	-	-	-	-	-	2.0	-	-
AE <sub>3</sub>	-	-	-	-	-	-	-	1.0	0.5
Carbonate	-	-	-	-	4.0	1.0	1.0	1.0	-
Sodium citrate	-	-	-	-	-	-	-	-	5.0
CFAA	-	-	-	-	-	-	-	-	-
Citric acid	-	-	-	-	-	4.0	-	1.0	1.0



QEA	-	-	-	-	-	2.0	2.0	1.0	-
SRP	-	-	-	-	-	1.0	1.0	0.2	-
Zeolite A	-	-	-	-	-	15.0	26.0	15.0	16.0
Sodium silicate	-	-	-	-	-	-	-	-	-
PEG	-	-	-	-	-	-	4.0	-	-
<u>Builder Agglomerate</u>									
SKS-6	6.0	5.0	-	-	6.0	3.0	-	7.0	10.0
LAS	4.0	5.0	-	-	5.0	3.0	-	10.0	12.0
<u>Dry-add particulate components</u>									
Effervescence Particle A	8.0		4.0	4.0	-		2.0	2.0	4.0
Effervescence Particle B		10.0							
Effervescence Particle D						8.0			
QEA	-	-	-	0.2	0.5	-	-	-	-
NACAOBS	3.0	-	-	1.5	-	-	-	2.5	-
NOBS	-	3.0	3.0	-	-	-	-	-	5.0
TAED	2.5	-	-	1.5	2.5	6.5	-	1.5	-
MBAS	-	-	-	8.0	-	-	8.0	-	4.0
LAS (flake)	-	-	-	-	-	-	-	8.0	-
<u>Spray-on</u>									
Brightener	0.2	0.2	0.3	0.1	0.2	0.1	-	0.6	-
Dye	-	-	-	0.3	0.05	0.1	-	-	-
AE7	-	-	-	-	-	0.5	-	0.7	-
Perfume	-	-	-	0.8	-	0.5	-	0.5	-

Dry-add									
Citrate	4.0	-	3.0	4.0	-	5.0	15.0	-	5.0
Percarbonate	15.0	3.0	6.0	10.0	-	-	-	18.0	5.0
Perborate	-	-	-	-	6.0	18.0	-	-	-
Photobleach	0.02	0.02	0.02	0.1	0.05	-	0.3	-	0.03
Enzymes (cellulase, amylase, protease, lipase)	1.5	0.3	0.5	0.5	0.8	2.0	0.5	0.16	0.2
Carbonate	-	-	-	-	-	5.0	8.0	10.0	5.0
Perfume (encapsulated)	0.6	0.5	0.5	-	0.3	0.5	0.2	0.1	0.6
Suds suppressor	1.0	0.6	0.3	-	0.10	0.5	1.0	0.3	1.2
Soap	0.5	0.2	0.3	3.0	0.5	-	-	0.3	-
Citric acid	-	-	-	6.0	6.0	-	-	-	5.0
Dyed carbonate (blue, green)	0.5	0.5	-	2.0	-	0.5	0.5	0.5	1.0
SKS-6	-	-	-	4.0	-	-	-	6.0	-
Fillers up to 100%									

Stability data was obtained by measuring suds produced by the respective composition due to the effervescence particle (1) immediately after preparation and (2) after 2 weeks storage at 27°C and 60% RH. Examples showed that as the eRH of the detergent matrix increased, there was a marked depletion in the suds produced after the two weeks storage, indicating that the stability of the effervescing components was poor. In contrast, the data showed that where the eRH of the matrix was reduced, the difference in suds level between test (1) and test (2) was significantly improved.

#### Example 7

A Spray dried granule having the composition setout in Table 4 (columns A-D) below is produced by forming an aqueous slurry which is then dried in typical spray drying tower to form low density granules. The granule is then compacted in a roller compactor (e.g., Shinto<sup>TM</sup>) and ground (by any grinder, for example Fitz<sup>TM</sup> Mill or hammer mill) to form high density particulates. The ground particulate is coated in

plough mixer (for example, Loedige™ KM) using aqueous (e.g., LAS/H<sub>2</sub>O) or non-aqueous binder (e.g., PEG-600) and dusted with AC-base. If needed, the coated particulate is dried in fluid bed to reduce moisture/eRH.

The coated particulate is mixed with a low level of non-compacted, low density granules. The low density granule is also made via same spray drying tower process and can be same or different spray dried granule. Other dry-admixes are added and perfume is sprayed in a low shear mixer (cement mixer, drum mixer, or Fukae™ mixer)

#### **Example 8**

The coated particulate whose process is described in Example 7 and formula as described in Table 4 (Column E). The coated particulate is mixed with the Builder Agglomerate from Example IIIB (but sieved to get 200microns mean particle size). Other dry-admixes are added and perfume is sprayed in a low shear mixer (cement mixer, drum mixer, or Fukae™ mixer)

**TABLE 4**

The following compositions are in accordance with the invention.

	A	B	C	D	E
<u>Spray-Dried then</u>					
<u>compacted Granules</u>					
LAS	16.0	8.0	10.0	8.0	16.0
MBAS	-	10.0	10.0	10.0	-
C <sub>45</sub> AS	4.0	2.0	-	2.0	4.0
Sodium carbonate	30.0	30.0	20.0	20.0	30.0
Sodium sulphate	0.0	5.0	5.0	5.0	0.0
Sodium silicate 1.6R	0.0	0.0	10.0	10.0	0.0
Zeolite A	5.0	5.0	5.0	5.0	5.0
MA/AA or AA	10.0	10.0	10.0	10.0	10.0
PEG 4000	1.0	1.0	1.0	1.0	1.0
Brightener	0.05	0.05	0.05	0.05	0.05

<u>Coating/Binder (of Spray-Dried Compacted Granules above)</u> <u>(Density 750g/L)</u> <u>(Mean particle size 600mm)</u>					
Zeolite A	5.0	5.0	5.0	5.0	5.0
PEG-600			3.0		
LAS	3.0	3.0	0	3.0	3.0
<u>Low density Spray-Dried Granules</u> <u>(Density 250g/L)</u> <u>(Mean particle size 300mm)</u>					
LAS	1.6	0.8	0.7	0.4	
MBAS	-	1.0	1.0	0.5	
C45AS	0.4	0.2	0.3	0.1	
Sodium carbonate	3.0	3.0	2.0	1.0	
Sodium sulphate	0	0.5	0	0.25	
Sodium silicate 1.6R	0	0	1.5	0.5	
Zeolite A	0.5	0.5	0.5	0.25	
MA/AA or AA	1.0	1.0	1.0	0.5	
PEG 4000	0.1	0.1	0.1	0.05	
Brightener	0.005	0.005	0.005	0.0025	
<u>Builder Agglomerate</u> <u>600g/L, (Sieved, 200 microns mean particle size)</u>					
LAS					3.5
SKS					3.5

<u>Dry-add particulate components</u>					
Effervescence Particle A	10.0		4.0		10.0
Effervescence Particle B		5.0		5.0	
Effervescence Particle D					
QEA	-	-	-	-	-
NOBS	-	3.0	3.0	3.0	-
TAED	2.5	-	-	-	2.5
Percarbonate	3.0	3.0	3.0	3.0	3.0
Enzymes (cellulase, amylase, protease, lipase)	1.5	0.3	0.5	0.3	1.5
Perfume (encapsulated)	0.6	0.5	0.5	0.5	0.6
Suds suppressor	1.0	0.6	0.3	0.6	1.0
Fillers (incl. H2O) up to 100%					

Fizz Suds evaluation was conducted where (1) the non-compacted, low density granule was added, and 2) the low density granule was NOT added. Data showed suds was much higher and lasted longer for (1) vs.(2).

5

Fizz Suds evaluation was also conducted where (1) the builder agglomerate (sieved to 200microns mean particle size) was added, and 2) the sieved builder agglomerate was NOT added. Data showed suds was much higher and lasted longer for (1) vs.(2).

10

## Claims

1. A detergent composition consisting essentially of an effervescence granule and a detergent matrix, characterised in that the detergent matrix has an eRH of no greater than 30 %.
- 5 2. A detergent composition according to claim 1 in which the detergent matrix has an eRH of no greater than 20%.
3. A detergent composition according to claim 1 or claim 2 in which the effervescence granule comprises two reactants which react with one another in the presence of water to release a gas and optionally additional stabilisers.
- 10 4. A detergent composition according to any preceding claim in which the detergent matrix comprises surfactant, builder and enzyme detergent ingredients.
5. A detergent composition comprising an effervescence granule and a detergent matrix in which the effervescence granule has an overall moisture content below 1 wt% and a moisture pick up no greater than 3% as measured at 60% RH and at 25°C to moisture  
15 equilibrium.
6. A detergent composition according to claim 5 in which the detergent matrix has an eRH of no greater than 30%.
7. A detergent composition according to any preceding claim in which the detergent matrix comprises at least one over-dried component.
- 20 8. A detergent composition according to any preceding claim in which the detergent matrix comprises a detergent matrix component which comprises a pre-formed surfactant-containing particle and optional additional detergent ingredients.
9. A detergent composition according to any preceding claim in which the detergent matrix component is the over-dried component.
- 25 10. A detergent composition according to any preceding claim in which the detergent matrix component comprises a spray dried particle.
11. A detergent composition comprising an effervescence particle and a low density detergent matrix component having a bulk density below 400 g/l.
12. A detergent composition according to claim 11 in which the median particle size of  
30 the low density detergent matrix component is from 50 to 500µm.

13. A detergent composition comprising an effervescence particle and a small particle size detergent matrix component having a bulk density from 400 to 800 g/l, and having a median particle size from 50 to 300  $\mu\text{m}$ .
14. A process for manufacturing a detergent composition comprising a detergent matrix and an effervescence particle, the detergent matrix comprising a detergent matrix component and optional additional detergent ingredients, the process comprising forming a detergent matrix component comprising surfactant by agglomeration and/or spray-drying and/or extrusion and/or marumerisation and/or compaction, submitting the detergent matrix component to a drying step, mixing the detergent matrix component and other optional additional detergent ingredients with the effervescence particle, wherein the eRH of the detergent matrix is below 30%.
15. A process according to claim 14 in which the detergent matrix component is prepared by a spray-drying process.
16. A process for manufacturing a detergent composition according to claim 14 or claim 15 in which the free moisture of the detergent matrix component is no greater than 0.05 wt%.
17. A process for manufacturing a detergent composition comprising a detergent matrix and an effervescence particle, the detergent matrix comprising a detergent matrix component and optional additional detergent ingredients, the process comprising forming a detergent matrix component comprising surfactant having a bulk density no greater than 400g/l and mixing with an effervescence particle and optional additional detergent ingredients.
18. A process according to claim 17 in which the detergent matrix component having a bulk density no greater than 400g/l is prepared in a spray drying or fluid bed agglomeration step.
19. A method for washing soiled surfaces comprising dissolving the detergent composition of any of claims 1 to 10 in an aqueous solution and contacting the solution with the soiled surfaces for washing.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/29294

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D3/00 C11D17/00 C11D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 3 769 224 A (INAMORATO J) 30 October 1973 (1973-10-30) column 4, line 45 - line 50; claim 1; example 2	11,12, 17-19 1,3-5, 7-10, 13-15
X A	WO 98 46715 A (PROCTER & GAMBLE) 22 October 1998 (1998-10-22) page 3, paragraph 2 - paragraph 3 page 42, paragraph 5 -page 43, paragraph 4; claims 3,13,14; example 1	13,19  1,3-5, 7-12, 14-18
Y A	EP 0 872 544 A (PROCTER & GAMBLE) 21 October 1998 (1998-10-21)  claims 1,9,10; examples A-F	1-4,8, 10,14, 15,17-19 5-7,9, 11-13,16



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*G\* document member of the same patent family

Date of the actual completion of the international search

2 February 2001

Date of mailing of the international search report

08/02/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Saunders, T



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/29294

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 92 06163 A (PROCTER & GAMBLE) 16 April 1992 (1992-04-16)	1-4, 8, 10, 14, 15, 17-19
A	page 17, paragraph 2 page 28, paragraph 2 -page 30, paragraph 2; examples 1A, 1B ---	5-7, 9, 11-13, 16
A	WO 95 05445 A (UNILEVER) 23 February 1995 (1995-02-23)  page 5, line 19 -page 6, line 5 page 15, line 6 -page 17, line 24 -----	1, 2, 4-11, 13-19

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/29294

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3769224 A	30-10-1973	AT 309639 B BE 733903 A CH 517174 A DE 1926084 A FR 2009985 A GB 1275596 A NL 6908319 A ES 367798 A	15-07-1973 03-11-1969 31-12-1971 04-12-1969 13-02-1970 24-05-1972 02-12-1969 16-04-1971
WO 9846715 A	22-10-1998	EP 0872544 A GB 2334962 A AU 6514898 A AU 6514998 A AU 6515198 A BR 9808551 A BR 9808894 A BR 9808895 A CN 1259991 T CN 1259992 T CN 1260827 T EP 0975722 A EP 0975723 A EP 0975724 A HU 0000936 A WO 9846714 A WO 9846716 A ZA 9803120 A ZA 9803121 A ZA 9803124 A	21-10-1998 08-09-1999 11-11-1998 11-11-1998 11-11-1998 23-05-2000 01-08-2000 01-08-2000 12-07-2000 12-07-2000 19-07-2000 02-02-2000 02-02-2000 02-02-2000 28-09-2000 22-10-1998 22-10-1998 17-05-1999 20-10-1998 28-06-1999
EP 0872544 A	21-10-1998	AU 6514898 A AU 6514998 A AU 6515198 A BR 9808551 A BR 9808894 A BR 9808895 A CN 1259991 T CN 1259992 T CN 1260827 T EP 0975722 A EP 0975723 A EP 0975724 A HU 0000936 A WO 9846714 A WO 9846715 A WO 9846716 A ZA 9803120 A ZA 9803121 A ZA 9803124 A	11-11-1998 11-11-1998 11-11-1998 23-05-2000 01-08-2000 01-08-2000 12-07-2000 12-07-2000 19-07-2000 02-02-2000 02-02-2000 02-02-2000 28-09-2000 22-10-1998 22-10-1998 22-10-1998 17-05-1999 20-10-1998 28-06-1999
WO 9206163 A	16-04-1992	AT 176801 T AU 8714891 A CA 2093438 A,C CN 1061433 A,B CZ 9300595 A DE 69130907 D DE 69130907 T DK 591203 T	15-03-1999 28-04-1992 07-04-1992 27-05-1992 15-06-1994 25-03-1999 09-09-1999 10-05-1999

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/29294

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9206163 A		EP 0591203 A	13-04-1994
		ES 2129412 T	16-06-1999
		FI 931526 A	02-06-1993
		HU 64388 A	28-12-1993
		IE 913498 A	08-04-1992
		JP 6501973 T	03-03-1994
		MX 9101473 A	05-06-1992
		NO 931276 A	07-06-1993
		NZ 240124 A	27-06-1995
		PT 99158 A	30-09-1992
		SK 31093 A	12-01-1994
		US 5482642 A	09-01-1996
WO 9505445 A	23-02-1995	AU 700040 B	17-12-1998
		AU 7532694 A	14-03-1995
		AU 9048098 A	07-01-1999
		BR 9407258 A	24-09-1996
		CA 2164107 A	23-02-1995
		CZ 9600458 A	12-06-1996
		DE 69409531 D	14-05-1998
		DE 69409531 T	20-08-1998
		EP 0714432 A	05-06-1996
		ES 2115967 T	01-07-1998
		HU 74078 A, B	28-10-1996
		JP 2925741 B	28-07-1999
		JP 9500926 T	28-01-1997
		PL 313039 A	27-05-1996
		SK 20896 A	09-07-1997
		TR 28735 A	20-02-1997
		ZA 9405591 A	29-01-1996

